

THE OFF-LINE AND ON-LINE ANALYSIS OF EFFLUENTS GENERATED DURING CONFINED PYROLYSIS OF ORGANIC MATTER

Patrick LANDAIS

Laurence GERARD and Laurence MANSUY
CNRS-CREGU - BP 23 Vandoeuvre Cedex. FRANCE

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INTRODUCTION

Confined system pyrolysis using gold tubes in cold-sealed pressurized autoclaves has proven his efficiency for simulating the main transformations of organic matter during thermal maturation (1), (2). However, these pressurized experimental systems are still poorly adapted to the quantitative analysis of effluents generated during pyrolysis. Indeed, until now, the acquisition of mass balances required fractionations of effluents into several classes and frequently induced the evaporation losses of volatile components.

In order to overcome such analytical problems, two new techniques have been designed and developped. The off-line analysis is a thermodesorption-multidimensional gas chromatograph which allows quantitative evaluation, in a single injection, of the amounts of CO₂, CO, N₂, H₂S, H₂O, C₁-C₃₀ hydrocarbons after gold-tube piercing. The on-line technique couples confined pyrolysis and analytical devices by means of a dual-oven allowing effluents pressure recording and continuous analysis of effluents by GC or GC-IR-MS during thermal maturation.

Description and applications of these two techniques are presented in this paper.

THERMODESORPTION-MULTIDIMENSIONAL GAS CHROMATOGRAPHY

This analytical system is constituted by a thermodesorption oven connected to a multidimensional gas chromatograph (Figure 1). The thermodesorption system is composed of a specially designed piercing device connected to a high temperature Valco C6UWT gas sampling valve via a series of valves which allow the sampling system to be evacuated and calibration gases or calibration liquid hydrocarbons mixtures to be injected. This sampling part is placed into a thermostated oven providing a homogeneous temperature of 250°C. A pressure transducer connected to a -1/0 bar vacuummeter measures the vacuum level in the sampling zone before piercing. A high temperature pressure transducer connected to a 0/16 bar manometer measures the effluent pressure in the sampling zone after piercing and before injection. The 0.5 ml injection loop of the Valco valve is connected to the chromatograph by a capillary fused silica transfer line heated at 280°C (carrier gas: H₂).

The two ovens of the Siemens Sichromat 2-8 multidimensional GC have their own temperature control and program which facilitate the installation of two capillary columns (oven 1: OV1, 50 m • 0,32 mm; oven 2: paraplott Q, 23 m • 0,32 mm) connected together by a pneumatic live switching system. A selected portion of the column 1 effluent containing partially resolved components (Ar, CO₂, CO, H₂S, H₂O, N₂, C₁-C₆) is transferred to column 2 for a complete separation and detection by a TCD. Other components (C₇-C₃₀) are separated by column 1 and directly transferred to a FID. Chromatographic data are recorded and processed by a ChemStation HP3365 software running on a HP Vectra computer.

The 5 cm long gold tube in which the kerogen has been pyrolysed is introduced in the piercing device. The sampling system is closed, evacuated and heated to 250°C before the gold tube is pierced. The thermovaporizable content of the tube expands into the evacuated sampling system and fills the sample loop. After an equilibration time of 30 min, the pressure is recorded by the manometer and the sample is injected into the chromatograph system. After each run, the gold tube is collected and weighed in order to determine the total weight loss. Calibration of H₂O and C₇-C₃₀ hydrocarbons is performed by injection of calibrated mixtures with a syringe. Gases are calibrated by direct injection of a calibration mixture into the sampling system.

Series of artificially matured kerogens from the Paris basin, the Mahakam Delta and the Woodford Shale have been obtained by confined pyrolysis at 250, 300, 350, 375, 400°C, 100M Pa in experiments lasting 24 and 72 hours. The pyrolyzates have been analyzed by TD-MDGC and subsequently CHCl₃ extracted.

On Figures 2a and 2b are represented the TD-MDGC FID and TCD traces of the 350°C pyrolyzate of an immature kerogen from Toarcian of the Paris Basin. The use of the selective transfer technique with columns of different polarity allows a good separation of the gases (TCD, b) and of the higher molecular weight hydrocarbons (FID, a).

Several results from TD-MDGC have been compared with data obtained by LC-GC of the high molecular weight components. Chromatographic distribution of *n*-alkanes as well as pristane/*n*C₁₇ ratios are similar. However, more accurate quantitative information is obtained on the C₇-C₁₂ and C₁-C₆ fractions. A complete mass balance for a series of artificially matured kerogens from the Toarcian of the Paris Basin is presented on Figure 3. The quantitative evolution of the different classes contribution relative to the initial organic matter weight clearly evidences the different phases of thermal maturation.

Comparison of TD-MDGC analysis of type II and type III series of maturation demonstrates their different behaviour especially when considering the amounts of CO₂, H₂O and gasolines generated during maturation. For example, late generation of CO₂ has been evidenced during the catagenetic phase of a type II kerogen.

Source-rocks pyrolyzates can also be directly analyzed by this technique.

PRESSURE RECORDING AND EFFLUENT SAMPLING DURING ARTIFICIAL MATURATION

Until now, the only pressure variations in the gold tube could be indirectly but continuously recorded. Preliminary results indicate a close correlation between effluents generation (gas + oil) and pressure variations. Furthermore, it is still impossible to differentiate the effects of secondary cracking from those of primary cracking.

So, a new pyrolysis system has been designed, allowing pressure recording and effluent sampling while preserving the characteristics of confined systems.

This device includes two separate ovens (Figure 4). The first one contains a 50 cc autoclave and a high temperature pressure transducer connected to a pressure recorder. The gold bag containing kerogen or source-rock (up to 10 g) is placed in the autoclave. An external pressure ranging between 0 to 100 MPa is applied on the bag through an argon pressurized line connected to an air-driven pump. A perfect gas-tight is assumed between the autoclave cell and the inside of the bag. This allows an absolute pressure record of the effluents released during pyrolysis. A micro-metering valve in the oven 1 and a pressure regulation valve in the oven 2 allows the transfer of an effluent aliquot toward the oven 2. In this second oven, a high temperature pressure transducer connected to a pressure recorder measures the effluent pressure in the 5 cc steel cell where the effluent are collected or in the sampling loop of the Valco C6UWT valve if the system is connected to a GC or a GC-IR-MS by a capillary fused silica transfer line heated at 360°C. In each oven, a blow-pipe valve connected to a vacuum pump allows the venting of the effluents at the beginning of the experiments and after each effluent sampling. The temperature is controlled by four K-thermocouples located in each oven, in the autoclave and in the furnace. The temperatures in the two thermostated ovens and in the furnace are regulated independently with a precision of $\pm 1^\circ\text{C}$ by an electronic system. The temperature is assumed to be homogeneous in the whole system. The effluent pressure variations are plotted against time by a graphic recorder.

The kerogen or the source-rock is placed in the gold bag and compacted. The bag is fixed to the autoclave and the external argon pressure is applied (0-100 MPa). The heating rate up to the isotherm temperature depends on the final temperature and range between 5 and 10 $^\circ\text{C}/\text{mn}$. The generated effluents are released in the pipe of the oven 1 and the pressure evolution is recorded. Aliquots are sampled at different time intervals: each 2 hours during the first day of pyrolysis and then at longer time intervals. For each sampling, the aliquots are evacuated toward the oven 2 whose temperature is the same as oven 1 in order to avoid any condensation. A constant volume of effluents is injected toward a GC by the Valco valve after measuring the pressure. The chromatograph analyses H_2O , CO , CO_2 , H_2S , N_2 and $\text{C}_1\text{-C}_{40}$ hydrocarbons in one single injection. The connection with an IR-MS will allow the precise typing of oxygenated functions, cyclic and aromatic compounds. After each sampling, the

residual effluents of the oven 2 are vented by opening the blow-pipe valve connected to the vacuum pump.

This new technique makes possible new experiments in confined medium:

- the large volume of the gold bag ($\varnothing = 1,5$ cm, $L = 5$ cm) facilitates source-rock pyrolysis and studies of organic/mineral interactions
- the sampling and venting facilities allow the studies of the expelled fraction in source-rock pyrolysis
- the differentiation between primary and secondary reactions can be done by venting the oven 1 after each sampling. So, the only effluents generated between two samplings are analysed and only primary cracking is considered. The secondary cracking can be studied by thermal maturation of the aliquot in the oven 2 (independent regulation) after each sampling.

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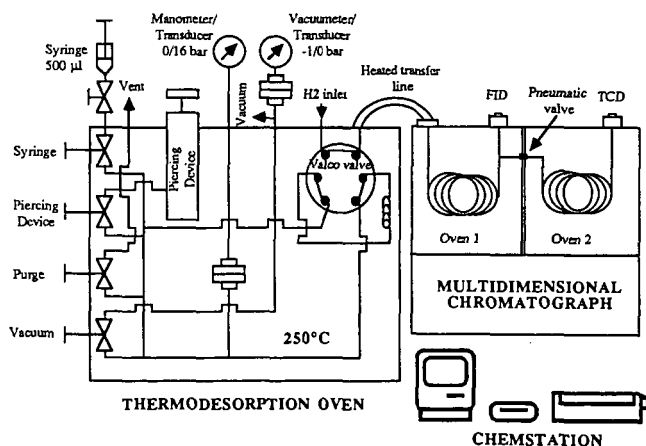


Fig.1. Scheme of the thermodesorption-multidimensional gas chromatography system

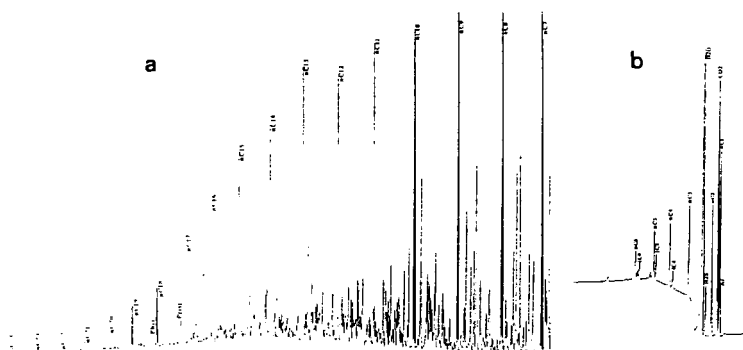


Fig. 2. TD-MDGC FID (a) and TCD (b) traces of the 350°C pyrolyzate of a Paris Basin kerogen.

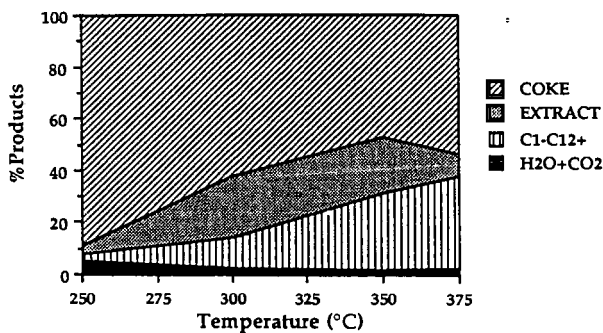


Fig. 3. Mass balance of a series of artificially matured kerogens from the Paris Basin.

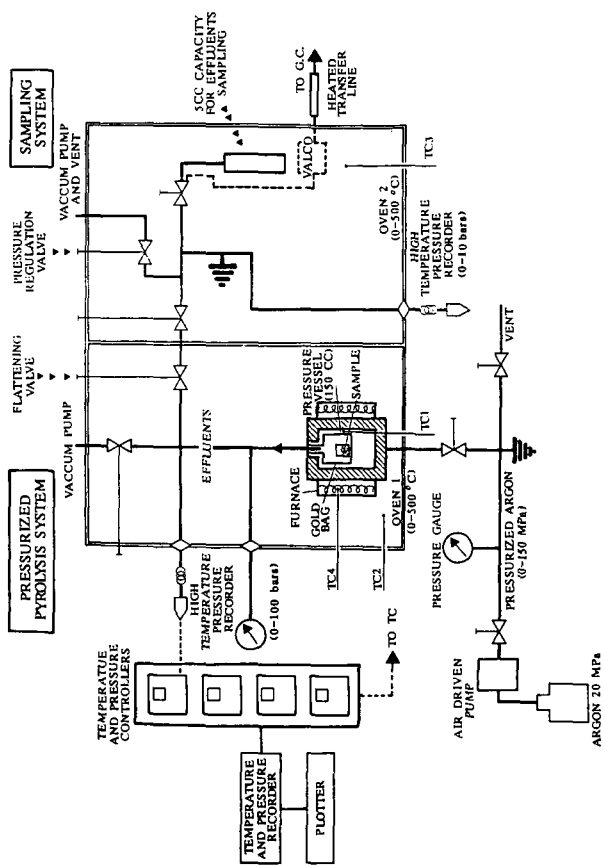


Fig. 4. Scheme of the pyrolysis and sampling systems in the new pressurized confined-pyrolysis device.